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DEVELOPMENT OF TECHNOLOGY FOR ENTRAINER-ENHANCED CO₂ FLOODING

Project BE5B, FY89 Annual Research Plan, Milestone 6

by Feliciano M. Llave

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DEVELOPMENT OF TECHNOLOGY FOR ENTRAINER-ENHANCED CO₂ FLOODING

By Feliciano M. Llave

ABSTRACT

The results of studies conducted to evaluate the development of the technology for utilizing entrainers for carbon dioxide (CO₂) flooding are described. Experiments were conducted to determine the extent of the fluid-property enhancement (gas-phase density and viscosity) of CO₂ + hydrocarbon and CO₂ + crude oil systems in the presence of selected entrainers (cosolvents). The improvement in CO₂-rich phase hydrocarbon extraction capacity was also determined in the presence of added cosolvents. The hydrocarbon systems used in the study were n-hexadecane and a crude oil sample from Bloomington (TX) field with an API gravity of 22.7°. The results of the experiments showed that the addition of cosolvents contributed to a significant enhancement in extraction of high-molecular weight components of the oil into the CO₂-rich phase. The degree of enhancement in component extraction was also dependent on the system pressure and amount of cosolvent added. Preliminary entrainer screening studies were conducted utilizing gas and liquid chromatographic approaches to determine relative affinities of certain cosolvents with target high-molecular-weight hydrocarbon solutes. These solutes ranged in molecular weights from n-decane (n-C₁₀) up to n-tetracontane (n-C₄₀). These qualitative screening methods were useful in identifying potential cosolvents that may be used for future study.

A method of utilizing entrainers to enhance the extraction of polymeric materials into the CO₂-rich phase was also investigated. This approach utilized a simple extraction apparatus to determine relative degrees of polymer extraction in CO₂ as a function of pressure and the degree of enhancement of extraction in the presence of added cosolvent. The results indicate the potential of using cosolvents in enhancing the solubility of polymeric materials into the CO₂-rich phase. The solubility of a polymer sample was increased by as much as two times when a cosolvent was added to the system, compared to conditions when using CO₂ alone. Additional work will be needed in order to properly select cosolvent-polymer combinations and to determine optimum conditions where enhancement in polymer solubility can result in substantial improvement in the CO₂-rich phase bulk fluid properties.

INTRODUCTION

The successful application of gas flooding processes, such as CO₂ flooding, for oil recovery depends on the ability of the injected gas to come in contact with the oil. Carbon dioxide flooding processes have a potentially high displacement efficiency. However oil recovery efficiency can be significantly hindered by the unfavorable mobility of the gas with respect to that of the oil. Under normal reservoir conditions, because the injected gas is considerably less viscous and has a lower density than

the target oil being displaced, which has a tendency to by-pass the oil which results in poor sweep efficiency and early gas breakthrough.

Carbon dioxide flooding has been used to recover both light and heavy oils. The CO₂ gas flooding processes involve two variations: miscible and immiscible. Both processes suffer significantly from the unfavorable mobility ratio of the gas with respect to the oil. The mobility control problem is even compounded whenever a highly viscous (heavy) oil is the target for recovery. There is a greater need for mobility control when CO₂ is used to recover the more viscous crude oils. Research efforts within the petroleum industry have been focused on finding ways to mitigate the problem of unfavorable gas mobility. Methods discussed in the literature include (1) utilizing the water-alternate-gas (WAG) process; (2) using foams; (3) viscosifying the CO₂-phase by means of adding polymers as direct thickeners,¹⁻² or (4) in situ polymerization of monomers that may be soluble in supercritical carbon dioxide.³ More recently, methods involving reverse micellar formations have also been investigated in supercritical fluid systems.⁴

Our efforts to mitigate the problem of gas mobility control have been focused on the method of adding a small amount of a soluble component, an entrainer, to pure supercritical solvents such as CO₂ in an effort to improve the solvent power of the gas. Preliminary results have shown the potential of utilizing entrainers in improving the recovery efficiency of CO₂ flooding.⁵⁻⁷ The results indicated that the addition of suitable entrainers preferentially increased the extraction of the heavier components of a synthetic oil as well as the density and viscosity of the CO₂-rich phase.

This status report summarizes the results of studies conducted to evaluate the development of the technology utilizing entrainers for CO₂ flooding. Experiments were conducted to test the potential of enhancing the density and viscosity of CO₂ by the addition of representative entrainers. The systems tested include a CO₂ + hydrocarbon system and CO₂ + crude oil system. The results of both studies indicate that the addition of entrainers significantly improved the extraction of the high-molecular-weight hydrocarbon components. Screening studies were conducted to evaluate additional cosolvents for their potential use as entrainers. The studies were performed by a method utilizing gas and liquid chromatography methods to determine the relative affinities of candidate entrainers with different high-molecular-weight hydrocarbons ranging from n-decane (n-C₁₀) up to n-tetracontane (n-C₄₀).

An initial evaluation of the potential for the use of entrainers to improve the solubility of polymers in CO₂ was also investigated. The use of polymers as direct thickeners for CO₂ flooding have a significant potential in improving gas mobility. The primary difficulty in this mobility control approach is finding a suitable polymer that is soluble enough in CO₂ to impart a significant enhancement in the gas phase viscosity and density. Extensive studies have been reported in the literature without any success in finding a commercially viable direct thickener for CO₂.¹⁻² Our present study was conducted to evaluate

the potential merit of utilizing entrainers to improve the solubility of polymeric materials in the CO₂-rich phase.

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ENTRAINER-ENHANCED CO₂ SUPERCRITICAL EXTRACTION

Experimental Apparatus and Procedure

An apparatus was constructed to measure the solubility of hydrocarbons and polymers in CO₂ and the resulting increase in viscosity of the CO₂-rich phase after the addition of an entrainer (cosolvent) at high pressures and temperatures. The new equipment provided the capability to measure compositions of both gas and liquid phases. Measurements of the viscosities and densities of the two phases were also possible. This new design provided a significant improvement to the experimental set-up used for the FY88 work.⁷ The new design allowed for both liquid and gas phase properties to be determined. Provision for polymer solubility measurements have also been incorporated in the design.

The apparatus, as shown in figure 1, consisted of a high-pressure dual-drive pump, high-pressure floating piston vessels, high-pressure windowed cells, capillary tubings, density meter, magnetic circulating pump, high-pressure sampling valve assembly, pressure gauge, pressure transducers, and transmitters. Major components of the apparatus were housed in a constant-temperature oven. Temperatures at various points within the oven were measured using copper/constantan thermocouples connected to a digital temperature monitor. A high-pressure windowed cell (100 cm³) was used as the equilibrium cell for the experiments. A magnetic circulating pump was also provided for vapor or liquid phase circulation. A high-pressure sampling valve was installed in the line to facilitate fluid (gas or liquid) sampling. The phase compositions were analyzed using a gas chromatograph with both thermal conductivity (TCD) and flame ionization detectors (FID). Fluid densities were measured using an in-line density meter. Two capillary tubes were used for the construction of the capillary viscometers. The combination of the floating piston vessels and the dual-drive pump permitted measurements of phase viscosities. This capillary tube viscometer design was of the modified Rankine type viscometer. The pressure gradient across the capillary tubing was accurately measured using differential pressure transmitters. The densities and viscosities of carbon dioxide (at 122.0° C and 2,000 psig) and nitrogen (at

FIGURE 1. - Schematic diagram of multiproperty measurement apparatus.

25.0° C and 2,200 psig) were determined using the new design. The results were in agreement with literature data to within ± 1 % for both gases.

The experiments were conducted by injecting a measured amount of the target solute (hydrocarbon or crude oil) into the evacuated equilibrium cell. A known amount of the selected entrainer was then injected into the equilibrium cell. The system's pressure was adjusted by injecting compressed CO₂ into the cell at the test pressure conditions. Upon reaching equilibrium, the gas phase viscosity and density were measured using the capillary viscometer and the remote density cell. Several measurements were conducted for each experiment to determine an average measurement for the gas phase properties. The composition of the gas phase was determined using the in-line sampling valve connected directly to the GC apparatus. Different pressures were tested for each sample loading to determine the pressure dependence of the fluid properties and composition. Several concentrations of entrainers were also used to determine the dependence of the enhancement in solvent extraction power on entrainer concentration. The specifics of the procedure for determining viscosities and densities were discussed in a previous report.⁷

Experimental Results and Discussion

The density and viscosity of the CO₂-rich phase for the system of CO₂ + n-hexadecane was determined as a function of pressure at 60° C. The study was conducted to investigate the enhancement in bulk properties of the CO₂-rich phase with the addition of suitable entrainers. Experiments using n-hexadecane also served a two-fold purpose: (1) comparison with available literature data⁸ on n-hexadecane and CO₂ at 60° C; and (2) determination of multiple-phase properties at entrainer-enhanced conditions. The solubility of n-hexadecane in CO₂ was determined with the presence of entrainers. The results are presented in figures 2 and 3. Figure 2 shows a plot of the CO₂-rich phase viscosity as a function of pressure with and without the entrainer added. The cosolvents used for the experiments were isooctane (i-C₈) and 2-ethylhexanol (2-EOH). The binary systems of CO₂ + 2-ethylhexanol and CO₂ + isooctane formed a single phase fluid under the conditions tested. The results of the experiment showed that the presence of the entrainers (isooctane or 2-ethylhexanol) enhanced the viscosity of the CO₂-rich phase. The plots show the extent of the difference in CO₂-rich phase viscosity by comparing literature values for the viscosity⁹ of pure CO₂ to that of CO₂ + n-hexadecane system with and without entrainers.

Figure 3 shows a plot of the CO₂-rich phase density as a function of pressure. The plots show the difference in measured density of the systems studied. The presence of the cosolvents contributed to an increase in CO₂-rich phase density. The transition points noted in the two figures were observed phase behavior relatively close to a transition from a two-phase system to a single-phase system. Single-phase data points are labeled accordingly. Table 1 lists a sample comparison of the enhancement effect of the

FIGURE 2. - Measured gas viscosity versus pressure for CO₂ + n-hexadecane at 60° C.

FIGURE 3. - Measured gas density versus pressure for CO₂ + n-hexadecane at 60° C.

TABLE 1. - Comparison of entrainer-enhanced gas phase properties at 60° C and 2,200 psig

	Viscosity	Density	Mole frac. n-C ₁₆ ¹
Pure CO ₂ ²	0.0421	0.5500	n. a.
CO ₂ + n-C ₁₆	0.0463	0.5824	0.0216
% inc. from pure CO ₂	9.8 %	5.9 %	-----
CO ₂ + n-C ₁₆ + isooctane	0.0524	0.6256	0.0623
% inc. from pure CO ₂	24.4 %	13.8 %	-----
% inc. from CO ₂ + n-C ₁₆	13.2 %	7.4 %	188.4 %
CO ₂ + n-C ₁₆ + 2-ethylhexanol	0.0619	0.6542	0.0437
% inc. from pure CO ₂	47.0 %	19.0 %	-----
% inc. from CO ₂ + n-C ₁₆	33.8 %	12.3 %	102.3 %
% inc. from CO ₂ + n-C ₁₆ + isooctane	18.2 %	4.6 %	-29.9 %

¹Entrainer-free basis.²Literature data: Vargaftik.¹⁰

corresponding entrainer on the solubility of n-hexadecane and the properties of the CO₂-rich phase. Comparing the viscosities of the systems studied, the addition of the isooctane resulted in viscosity increases of about 25% above those of pure CO₂, and the 2-ethylhexanol addition resulted in increases in viscosity of about 47%. The addition of isooctane resulted in a density increase of about 14% over that of pure CO₂, while the addition of the alcohol resulted in a density increase of about 19%. The effects of the entrainers on the fluid properties came from two factors: (1) the direct solubility of the more viscous and dense entrainer, and (2) the enhancement in the extraction of the hydrocarbon in the CO₂-rich phase. The addition of isooctane enhanced the extraction of n-hexadecane by about 190% compared to the alcohol which increased the extraction of n-hexadecane by about 102%. This comparison shows that although the alcohol addition resulted in a lesser degree of hydrocarbon-extraction enhancement, compared to the effect of isooctane, the addition of alcohol entrainer to the CO₂-rich phase resulted in a higher viscosity and density because of its greater viscosity and density compared with that of isooctane.

The properties of the CO₂-rich phase for the system of CO₂ + crude oil (Bloomington oil, 22.7 °API) were determined as a function of pressure at 50° C. The study was conducted to determine the enhancement in bulk properties of the CO₂-rich phase in the presence of entrainers. The results are presented in figures 4 and 5. Figure 4 shows a plot of the CO₂-rich phase viscosity as a function of

FIGURE 4. - Measured gas viscosity versus pressure for CO₂ + crude oil (22.7° API) at 50° C.

FIGURE 5. - Measured gas density versus pressure for CO₂ + crude oil (22.7° API) at 50° C.

pressure with and without added entrainer. The cosolvent used for the experiments was isooctane. Two entrainer concentrations were tested to determine the effect on the enhancement of gas-phase properties. The binary system of CO₂ + isooctane alone formed a single-phase fluid under the conditions tested. The results of the experiments showed that the presence of the entrainer (isooctane) increased the viscosity of the CO₂-rich phase. The plot shows the extent of the difference in CO₂-rich phase viscosity by comparing literature values for the viscosity⁹ of pure CO₂ to that of the CO₂ + crude oil system with and without added entrainer. Figure 5 shows a plot of the CO₂-rich phase density as a function of system pressure. The presence of the cosolvent contributed to a slight increase in CO₂-rich phase density.

The composition of the CO₂-rich phase was also determined with the presence of entrainers. Figure 6 shows a plot of the GC detector signal level as a function of retention time. The plot shows the distribution of the hydrocarbon components in the gas phase. Three experiments conducted at 50° C and about 1,780 psi are depicted in this figure. One shows a trace of the experiment using CO₂ alone, while the other two experiments involved loadings of 2.5 and 8.0 mol % isooctane in CO₂. The figure clearly shows the difference in the hydrocarbon composition of the CO₂-rich phase in the three

FIGURE 6. - Extraction of high-molecular-weight components as a function of entrainer concentration.

experiments. The extraction of the heavy molecular weight hydrocarbons was considerably improved with the addition of the entrainer. The amount of heavy hydrocarbon components extracted increased as the concentration of isooctane was increased. The results of the experiments showed that using CO₂ alone, the highest hydrocarbon chain length detectable was the C₁₈ group. The addition of isooctane at 2.5 and 8.0 mol % increased the highest detectable hydrocarbon chain length to C₂₄ and C₃₆, respectively. There is a definite contribution from the addition of the entrainer to improving extraction of high-molecular-weight hydrocarbon components of the crude oil.

A comparison of the effect of pressure and the presence of entrainer is shown in figures 7 and 8. The cosolvent used in the experiments was isooctane. Figure 7 shows a plot of the GC detector signal level as a function of the retention time. The plot shows the hydrocarbon molecular weight distribution of the gas phase components. The plot shows that using CO₂ alone did not significantly alter the molecular-weight distribution of the components greater than n-octadecane, C₁₈. There was an indication of some difference in detectable signal levels for the higher-molecular-weight hydrocarbons from 1,798 to about 3,133 psi. Overall, despite of the difference in range of pressures, using CO₂ alone did not markedly improve the extraction of the high-molecular-weight hydrocarbons. Figure 8 shows a plot of the GC detector response as a function of the retention time when 8.0 mol % cosolvent was added to the system of CO₂ + crude oil. Compared to figure 7, the addition of the entrainer significantly improved the extraction of high-molecular-weight components. The addition of the entrainer enhanced the extraction capacity of the CO₂-rich phase to the extent that the highest extracted molecular weight hydrocarbon was shifted from about C₁₈ to about C₃₆ at a pressure of about 1,800 psi. The amount of heavy molecular weight components extracted was also significantly improved when the system pressure was increased from 1,778 to 2,850 psi, at the same entrainer concentration. The results indicate that increasing the pressure alone did not improve the level of heavy molecular weight component extraction when using only CO₂. On the other hand, the addition of the entrainer to the system of CO₂ + crude oil significantly increased the extraction of the high-molecular-weight components as a function of system pressure and entrainer concentration.

SCREENING METHOD FOR ENTRAINER EVALUATION

The selection of entrainers strongly depends on the reservoir operating conditions to be encountered. Cosolvents that have appreciable solubility in the gas phase and the ability to enhance the solubility of crude oil heavy components in the CO₂-rich phase would be positive factors in the selection. Our previous studies have concentrated on a limited number of cosolvents that have been found to be suitable for entrainer application. These cosolvents include hydrocarbons (i.e. isooctane) and alcohols (i.e. 2-ethylhexanol). In order to screen additional potential candidates as entrainers, quick screening methods were designed to provide a tool to select cosolvents that may be used in future experimental evaluations. The screening experiments were conducted investigate methods to determine cosolvent-

FIGURE 7. - Effect of pressure on extraction of high-molecular-weight components by using CO_2 .

FIGURE 8. - Effect of pressure on extraction of high-molecular-weight components by using CO_2 + cosolvent.

solute (high-molecular-weight hydrocarbon) affinity using gas chromatography (GC) and liquid chromatography (LC) method. The approach examines the effect of the cosolvent-solute combination in the absence of the primary solvent, CO₂.

Cosolvent screening using the GC method was conducted by comparing the retention times of different amounts of cosolvent injected in columns packed with different high-molecular-weight hydrocarbons at a uniform temperature of 50° C. The idea behind the screening method was based on the difference in the affinity of the cosolvents to the packing material in the column. The affinity of the cosolvent to the hydrocarbon packing material can be qualitatively determined by the difference in retention times of the cosolvents in each of the columns tested. The selection criterion for the candidate cosolvent is that the longer the retention time of a particular cosolvent in a target column, the greater the affinity of the cosolvent is for the hydrocarbon material used to pack the column. In each of the columns used, the primary packing material used was UCW-982 with a methyl silicone liquid phase. The difference in retention times was used as a qualitative indication of the relative degree of affinity of the cosolvent with the column media compared to the UCW-982 packing material alone. Experiments were conducted to determine the retention times of cosolvents on the following columns: (1) packed with 100 wt % UCW-982 packing material; (2) packed with only 33 wt % UCW-982 packing material with 67 % void space; (3) packed with 13 wt % n-triacontane, n-C₃₀, + 87 wt % UCW-982 packing material; (4) packed with 64 wt % n-C₃₀ + 36 wt % UCW-982 packing material; (5) packed with 46 wt % n-tetracontane, n-C₄₀, + 54 wt % UCW-982 packing material; and (6) packed with 68 wt % n-pentacosane, n-C₂₅ + 32 wt % UCW-982 packing material. The columns containing hydrocarbons were packed by filling the column with a known amount of the primary packing material UCW-982, followed by the powdered form of the target high-molecular-weight hydrocarbon. The hydrocarbon-filled portion of the column was connected to the injection side of the column, the UCW-982-filled section was connected to the detector side, with helium used as carrier gas. The results are presented as a ratio of the retention time with respect to a selected baseline (figs. 9 through 11). The baselines or reference lines used were the retention times of each of the cosolvents on the columns packed with 100 wt % UCW-982 packing material and one packed with only 33 wt % UCW-982 packing material and 67 % void space. Retention time ratios lower than 1 represent conditions where that in target column was significantly less than that in the reference column. Retention time ratios greater than 1 represent conditions where in the target column were significantly greater compared to those in the reference column.

A comparison of the ratio of the retention times of various cosolvents as a function of the amount of UCW-982 packing material in the column is shown in figure 9. The columns tested for this experiment were those packed with 100 wt % UCW-982 and packed with only 33 wt % UCW-982. The purpose of the experiment was to differentiate the effect of the amount of primary packing material used in the

column, UCW-982, on the retention times of the different cosolvents. The plot shows that most of the cosolvents show a proportional dependence on the quantity of UCW-982 packing material. The ratio of retention time closer to 0.33 indicates the expected dependence of the retention time of the cosolvent on the amount of UCW-982 packing material in the column, which was decreased to 33 wt % only. The amount of injected cosolvent, 0.1 to 0.5 μL did not significantly alter the retention times of the samples tested. A different behavior was observed though for several more polar cosolvents like ammonia, methanol, ethanol, and acetone. The retention times for these cosolvents remained almost the same even with a reduction in amount of UCW-982 packing material. Some other interaction besides the dependence on amount of packing material may be attributed to this behavior. Component decomposition could have occurred under the experimental conditions tested. This behavior may contribute to some problem or error in determining or ranking the affinity of these cosolvents for the hydrocarbon packed columns tested, such that these cosolvents will not be used in the cosolvent ranking process. Further tests will be needed to determine the factors that may have contributed to this difference in retention time behavior.

Figure 10 shows a comparison of the ratio of the retention times determined from each of the hydrocarbon-filled-column experiments. The reference for these results was based on the retention time

FIGURE 9. - Dependence of cosolvent retention times on amount UCW-982 packing material.

from the column packed with 100 wt % UCW-982. The results at first seems to indicate that, in general, most of the cosolvents tested followed the behavior of decreasing affinity in this order: $n\text{-C}_{30} > n\text{-C}_{40} \geq n\text{-C}_{25}$. This discrepancy in the affinity ranking may be attributed to the way the hydrocarbon packed columns may have been prepared. A difference in the manner of packing these columns, whether tightly or loosely packed, can contribute to a significant difference in retention times for each column. This difference will invalidate any possible ranking in hydrocarbon affinity order. Comparison of the cosolvents' affinity should be only be made with each individual high-molecular-weight hydrocarbon filled column. Figure 11 shows a comparison of the ratio of the retention times determined from each of the hydrocarbon filled column experiments. The reference for these results was based on the retention time from the column packed only with 33 wt % UCW-982 packing material. This figure provides a better qualitative picture of the relative degree of affinity of the cosolvents for each of the high-molecular-weight hydrocarbon components. Petroleum ether and 2-ethylhexanol showed greater affinity for the $n\text{-C}_{25}$ component compared to the other cosolvents using that column. The petroleum ether showed greater affinity for the $n\text{-C}_{30}$ component while 2-ethylhexanol showed greater affinity for the $n\text{-C}_{40}$ component compared to the other cosolvents using that column. For the $n\text{-C}_{40}$ column tests, the 2-ethylhexanol, petroleum ether and chloroform showed comparable affinity for the hydrocarbon component.

FIGURE 10. - Comparison of ratio of cosolvent retention times on different high-molecular-weight hydrocarbon packed columns, based on retention time from column packed with 100 wt % UCW-982.

Overall, the GC screening method has been useful in identifying other potential cosolvents that have particular affinity for a certain range of high molecular weight hydrocarbons. Cosolvents such as petroleum ether and chloroform may have potential application as entrainers. The more polar cosolvents such as ammonia, methanol, ethanol, and acetone need to further studied. The difference in retention time behavior dependence on amount of packing material present needs to be addressed. Additional experiments will be needed for that purpose. One limitation though of the GC screening method was that it was designed primarily to evaluate only the affinity of a cosolvent to a particular solute. The method does not take into account the effect of the presence of the CO₂ in the cosolvent-solute system. An ideal entrainer would have (1) appreciable solubility in the gas phase; (2) ability to enhance the solubility of crude oil components in the gas phase; (3) high viscosity; and (4) low solubility in water. The GC screening method was useful in qualitatively determining the potential of certain cosolvents to enhance the solubility of high molecular weight components. In order to further evaluate the selected cosolvents, other experiments have to be conducted to determine the solubility of the cosolvents in CO₂ and the degree of enhancement in gas phase density and viscosity that the cosolvent can impart to the CO₂-rich

FIGURE 11. - Comparison of ratio of cosolvent retention times on different high-molecular-weight hydrocarbon packed columns, based on retention time from column packed with 33 wt % UCW-982.

phase. Other experiments also have to be conducted to determine the ability of the selected cosolvents in enhancing the solubility of high molecular weight components of the oil in the gas phase. The combination of all these studies will be very useful in determining the potential application of these cosolvents.

A different cosolvent screening method using an LC was used to compare the retention times of different amounts of hydrocarbon samples injected in C₈ and C₁₈ based columns. The experiments were conducted using different ratios of ethanol and n-hexane as solvent pairs. The experiments were conducted to determine the relative degree of affinity of the hydrocarbon sample for the solvent mixture and the hydrocarbon based column. The experiments using the LC utilized a different approach in terms of ranking the hydrocarbon-cosolvent affinity compared to the GC experiments. In the LC experiments, the cosolvents were used as the mobile phase, while the material used for the column was either C₈ or C₁₈ based. In these experiments, the hydrocarbon sample containing n-decane, n-dodecane, n-tetradecane, and n-hexadecane or a combination of these hydrocarbons, was injected in the solvent stream. The retention times of the hydrocarbon in the different solvent mixtures were determined in order to observe the effect of the solvent pair concentration on the hydrocarbon retention times. The experiments provided a qualitative ranking of the affinity of the hydrocarbon sample for the hydrocarbon based column or the mobile phase solvent pair.

Two types of LC column packing materials were used in the study: one using a C₈ based packing material and another using a C₁₈ based material. In both sets of experiments, ethanol and n-hexane were used as solvents. Ethanol was chosen because of the comparable hydrocarbon affinity it exhibited in the GC screening conducted and because of its general use as an HPLC solvent. The n-hexane was chosen as the primary solvent because of its similarity of solvent properties with that of CO₂ at high pressure. The n-hexane + ethanol system was selected to provide a solvent pair that would emulate the dense phase supercritical CO₂ + cosolvent (ethanol) system.

The results of the experiments are presented in figures 12 through 14. The figures show the retention time of each of the hydrocarbon samples injected using a refractive index (RI) detector. The C₁₀-C₁₆ mixture used was an equal volume mixture of C₁₀, C₁₂, C₁₄, and C₁₆. In all experiments, only one chromatogram peak was detected for this C₁₀-C₁₆ mixture. The results presented in figure 12 showed no significant difference in retention time when using the solvent mixtures tested on the C₈ based column. The affinity of the injected hydrocarbon samples for the hydrocarbon based column and the solvent pairs were very similar, so that no difference in hydrocarbon retention times was observed. The affinity for the stationary phase material and the mobile phase material was too close to result in a difference in hydrocarbon sample retention time. The results showed that C₈ based column was not suitable for the experiments conducted. Figure 13 shows that by the use of a C₁₈ based column,

significantly higher retention times can be observed in comparison to that of a C₈ based column. Figure 14 shows a comparison of the different combination of solvent mixtures tested in the C₁₈ based column. These experiments were conducted to qualitatively determine the effect of solvent pair concentrations on the hydrocarbon sample retention times. The results indicated that a slight difference in retention times was achieved using a solvent mixture of 100% ethanol. On the other hand, no difference was observed when using 100% n-hexane only. When using a mixture of 70% ethanol and 30% n-hexane as solvent, a significant difference in retention times was observed. The retention times using the solvent pairs (70% ethanol and 30% n-hexane) were significantly higher than when using any of the solvents individually. On the other hand, the combination of 25% ethanol and 75% n-hexane as solvent did not show any significant retention time difference. The retention times were only slightly longer than when using 100% n-hexane as solvent. The system almost behaved similar to 100% n-hexane. The results for this solvent pair combination (25% ethanol and 75% n-hexane) were not presented in figure 14.

Within the limits of the solvent pair combinations tested, the results indicated that the combination of n-hexane and ethanol was not a good choice of solvent pair for the experiments conducted. The ideal

FIGURE 12. - Comparison of hydrocarbon retention time using different solvent mixtures in C₈ based column.

case would be a solvent mixture containing a primary solvent that behaves like CO₂ and the subsequent addition of a small amount of the secondary solvent significantly alters the retention times. Under those constraints, one would like a primary solvent that results in a significant difference in retention times for the hydrocarbon samples such that the addition of the secondary solvent results in a decrease in retention time which is indicative of a higher affinity of the sample towards the mobile phase. Our case was the reverse since we began with the initial condition of using 100% of the secondary solvent, ethanol, and subsequent addition of the primary solvent, n-hexane, resulted in the reduction of the retention times of the hydrocarbon samples. One important point to mention is that the affinity of the hydrocarbon samples for the hydrocarbon based columns and n-hexane was very similar such that no significant difference was observed. The proper selection of solvent pair would have resulted in a more promising result. Another modification to the LC approach to investigate would be to study the affinity of hydrocarbon samples that have molecular weights greater than that of the n-C₁₆. These higher molecular weight samples would provide a better gauge of the affinity difference of the hydrocarbon sample for the solvent phase or the hydrocarbon based column material.

FIGURE 13. - Comparison of hydrocarbon retention time using a C₈ and a C₁₈ based column.

FIGURE 14. - Comparison of hydrocarbon retention time using different solvent mixtures in a C₁₈ based column.

ENTRAINER-ENHANCED POLYMER SOLUBILITY IN CO₂

Extensive studies have been reported in the literature without any success in finding a commercially applicable polymer as direct thickener for CO₂ application. Our study provides an initial evaluation of the potential for the use of entrainers to improve the solubility of polymers in the gas phase. The objective would be to improve the solubility of the polymer in the CO₂-rich phase to an extent that a substantial increase in bulk CO₂-rich fluid properties can be achieved. This scoping study involved the determination of the extent of polymer solubility in the CO₂-rich phase with the addition of cosolvents. Figure 15 shows a schematic diagram of the experimental apparatus that was used to measure the amount of polymeric materials extracted under different conditions. High-pressure tubes packed with finely ground activated charcoal were used as the adsorption media for the extracted polymer materials. The experiments were conducted by injecting a measured amount of polymer into an evacuated high pressure floating piston vessel. A known amount of selected entrainer was then injected into the floating piston vessel when required. The pressure inside the vessel was adjusted by injecting compressed CO₂ into the vessel at the test pressure conditions. After sufficient time had been allowed for the system to reach equilibrium, the CO₂-rich gas phase was bled-off under constant pressure through the high-pressure tubes packed

with activated charcoal. A constant pressure CO₂-rich gas phase bleed was maintained throughout the sampling procedure by means of a high pressure direct drive pump injecting pressure fluid into the piston side of the floating piston vessel. The volume of CO₂ gas bled during the experiment was measured using a wet test meter. The gain in weight of the charcoal column accounts for the amount of polymeric material extracted into CO₂-rich phase. In experiments where cosolvents were added, the filtering media was purged with nitrogen under the same experimental temperature of 50° C in order to gradually remove the more volatile cosolvent that was trapped in the filtering media during the extraction experiment. A constant filter media weight was achieved after about several hours of nitrogen purging. These extraction experiments were conducted using CO₂ and CO₂ + cosolvent mixtures added to the polymer. Two industrial polymer samples were obtained and used in the experiments. The selection of the tested cosolvents though were done at random and were not based on any preliminary screening of cosolvent-polymer. The results of the experiments under each of the conditions tested are presented in table 2.

FIGURE 15. - Schematic diagram of polymer extraction apparatus.

TABLE 2. - Effect of entrainers on polymer solubility in the CO₂-rich phase at 50° C

Polymer	Cosolvent ¹	Pressure, psi	Solubility, g/L	% Increase
poly butene M.W.=320	none	3,000	3.100	n.a.
	isooctane	2,900	4.013	29.42
	2-ethylhexanol	3,000	3.597	16.03
	toluene	3,000	3.151	1.62
poly alpha olefin	none	3,000	0.582	n.a.
	isooctane	2,700	1.304	123.86
	2-ethylhexanol	2,700	1.561	168.08
	toluene	3,000	1.143	96.22
	benzene	2,900	1.112	90.94

¹ Cosolvent to Polymer Ratio = 1:4 at 4 vol% cosolvent loading

The results indicate that the addition of the entrainers did show a slight increase in the amount of material extracted. The extent of enhancement though may not be sufficient to significantly increase the viscosity and density of the gas phase. The results from the scoping study are preliminary, but they do indicate the potential of the use of entrainers in enhancing polymer solubility in the CO₂-rich phase. In order to determine optimum conditions and potential polymer-cosolvent combinations to make this method applicable, more thorough experimental studies will be necessary. These studies should involve (1) screening cosolvents for polymer solubility and compatibility; (2) testing the enhancement of the polymer solubility when using the cosolvents in the presence of CO₂; (3) measurement of the extent of the enhancement in CO₂-rich phase fluid properties with the addition of polymers; and (4) determining potential application problems under different conditions.

CONCLUSIONS

The objective of the study was to evaluate potential areas for the development of the technology for utilizing entrainers for carbon dioxide (CO₂) flooding. Experiments were conducted to determine the enhancement of the fluid-phase properties of CO₂ + hydrocarbon and CO₂ + crude oil systems in the presence of entrainers (cosolvents). The results showed that the presence of the entrainers (isooctane

or 2-ethylhexanol) can significantly enhance the viscosity and density of the CO₂-rich phase of the CO₂ + n-hexadecane and CO₂ + crude oil systems. The presence of the cosolvent contributed to an enhancement effect on the solubility of n-hexadecane and extraction of the high-molecular-weight components of the oil into the CO₂-rich phase. The enhancement in solubility was more pronounced in the case when using crude oil samples than when using single component high molecular weight hydrocarbons alone. The amount or concentration level of added entrainer also contributed to a significant difference in hydrocarbon extraction. The results showed that the addition of the entrainer at different concentrations increased the highest extractable hydrocarbon chain length from the crude oil. The system pressure did not significantly affect the extraction potential of the CO₂ phase without the addition of entrainers. With the addition of entrainers, the amount of heavy molecular weight components extracted was significantly increased when the system pressure was increased, even at the same entrainer concentration level. The results clearly showed that the addition of the entrainer to the system of CO₂ + crude oil significantly improved the extraction of the high-molecular-weight components as a function of system pressure and entrainer concentration.

The GC and LC screening methods have been useful in possibly qualitatively identifying other potential cosolvents that have particular affinity for a certain range of high molecular weight hydrocarbons. These initial experiments represent helpful steps in the effort to develop better and quicker means of evaluating potential entrainers. The results of the present study indicate that cosolvents such as petroleum ether and chloroform may have potential application as entrainers. The more polar cosolvents such as ammonia, methanol, ethanol, and acetone need to further studied. The difference in behavior for these cosolvents needs to be further investigated and additional experiments will be needed for that purpose. One limitation though of these initial screening methods was that they were designed primarily to evaluate only the affinity of a cosolvent to a particular solute. The method does not take into account the effect of the presence of the CO₂ in the cosolvent-solute system. Additional experiments have to be conducted to determine the solubility of the cosolvents in CO₂ and the degree of enhancement in gas phase density and viscosity that the cosolvent can impart to the CO₂-rich phase. Other screening methods have to be evaluated in order to develop better and faster means of testing other chemicals of cosolvent application potential.

Experiments were also conducted to determine the possibility of using entrainers to enhance the extraction of polymeric materials into the CO₂-rich phase. The results indicated the potential of using cosolvents in polymer solubility enhancement. The solubility of a polymer sample was increased by as much as two times when a cosolvent was added to the system, compared to conditions when using CO₂ alone. In these experiments, the gas phase viscosity was not experimentally measured such that the amount of enhancement in polymer solubility may or may not be sufficient to increase the viscosity and

density of the CO₂-rich phase significantly. Additional experimental work will be needed in order to properly select cosolvent-polymer combinations and to determine optimum conditions where the enhancement in polymer solubility can impart a substantial improvement in the CO₂-rich phase bulk fluid properties.

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